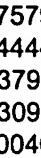
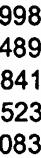


Cement admixture and cement composition

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 EP0757998
 EP0444489
 US5379841
 US4309523
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Abstract of EP1112982

A cement admixture comprising (A) a compound selected from a melaminesulfonic acid formaldehyde condensate, a naphthalenesulfonic acid formaldehyde condensate and salts thereof and (B) a copolymer obtained by copolymerizing a monomer mixture comprising (a) from 30 to 90 mass% of one or more N-vinylcarboxylic acid amide-type monomer represented by the formula (1) below, (b) from 10 to 70 mass% of one or more anionic unsaturated monomer selected from an unsaturated carboxylic acid-type monomer represented by the formula (2) below and an unsaturated sulfonic acid-type monomer represented by the formula (3) below, and optionally (c) from 0 to 40 mass% of one or more nonionic unsaturated monomer, provided that the total of (a), (b) and (c) is 100 mass%, wherein the symbols in the formulae are as described in the specification. <CHEM> <CHEM> CH₂=CR¹-NR²-C(=O)-R³ ... (1)



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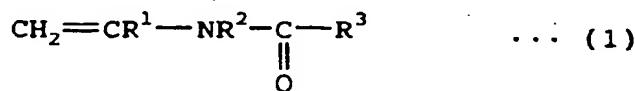
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(54) Cement admixture and cement composition

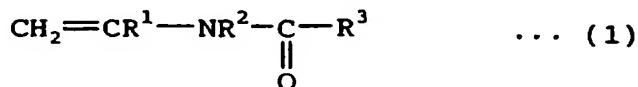
(57) A cement admixture comprising (A) a compound selected from a melaminesulfonic acid formaldehyde condensate, a naphthalenesulfonic acid formaldehyde condensate and salts thereof and (B) a copolymer obtained by copolymerizing a monomer mixture comprising (a) from 30 to 90 mass% of one or more N-vinylcarboxylic acid amide-type monomer represented by the formula (1) below, (b) from 10 to 70 mass% of one or more anionic unsaturated monomer selected from an unsaturated carboxylic acid-type monomer represented by the formula (2) below and an unsaturated sulfonic acid-type monomer represented by the formula (3) below, and optionally (c) from 0 to 40 mass% of one or more nonionic unsaturated monomer, provided that the total of (a), (b) and (c) is 100 mass%, wherein the symbols in the formulae are as described in the specification.



and a cement composition comprising said cement admixture are provided.

The cement admixture of the present invention can impart excellent capabilities to a fresh cement composition such as fluidity, fluidity retentive property, filling property and material separation resistance, therefore, can improve the quality of hardened form.

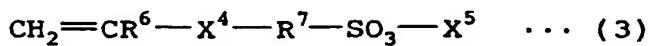
or more N-vinylcarboxylic acid amide-type monomer represented by the following formula (1)



wherein R¹, R² and R³ each independently represent hydrogen atom or a methyl group and
 (b) from 10 to 70 mass% of one or more anionic unsaturated monomer selected from an unsaturated carboxylic
 acid-type monomer represented by the following formula (2)



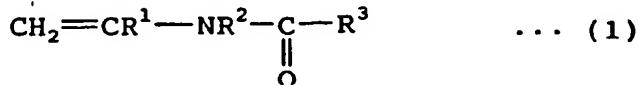
wherein R⁴ represents hydrogen atom, a methyl group or -COOX², R⁵ represents hydrogen atom, a methyl group or -COOX³, X¹, X² and X³ each independently represent hydrogen atom, an alkali metal, an alkaline earth metal, an ammonium group or an ammonium group substituted by an organic group, and n represents 0 or 1, provided that when n represents 0, R⁵ does not represent -COOX³ and
 an unsaturated sulfonic acid-type monomer represented by the following formula (3)



wherein R⁶ represents hydrogen atom or a methyl group, R⁷ represents a linear alkylene group having from 1 to 4 carbon atoms or a branched alkylene group, X⁴ represents -CONH- or -COO-, and X⁵ represents hydrogen atom, an alkali metal, an alkaline earth metal, an ammonium group or an ammonium group substituted by an organic group,
 provided that the total of (a) and (b) is 100 mass%.

2. A cement admixture comprising (A) one or more compound selected from a melaminesulfonic acid formaldehyde condensate, a naphthalenesulfonic acid formaldehyde condensate and salts thereof and (B₂) a copolymer obtained by copolymerizing a monomer mixture comprising

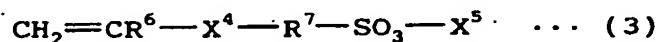
(a) from 30 to 90 mass% of one or more N-vinylcarboxylic acid amide-type monomer represented by the following formula (1).



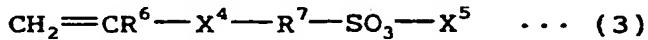
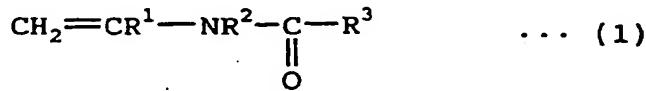
wherein the symbols have the same meanings as in 1 above,
 (b) from 10 to 70 mass% of one or more anionic unsaturated monomer selected from an unsaturated carboxylic acid-type monomer represented by the following formula (2)



wherein the symbols have the same meanings as in 1 above and
 an unsaturated sulfonic acid-type monomer represented by the following formula (3)



below and an unsaturated sulfonic acid-type monomer represented by the formula (3) below, provided that the total of (a) and (b) is 100 mass%; or (ii) a copolymer obtained by copolymerizing a monomer mixture comprising (a) from 30 to 90 mass% of one or more N-vinylcarboxylic acid amide-type monomer represented by the formula (1) below; (b) from 10 to 70 mass% of one or more anionic unsaturated monomer selected from an unsaturated carboxylic acid-type monomer represented by the formula (2) below and an unsaturated sulfonic acid-type monomer represented by the formula (3) below, and (c) from 0 to 40 mass% of one or more nonionic unsaturated monomer, provided that the total of (a), (b) and (c) is 100 mass%.



[0018] In the above formula (1), R¹, R² and R³ each independently represent hydrogen atom or a methyl group.

[0019] In the above formula (2), R⁴ represents hydrogen atom, a methyl group or -COOX², R⁵ represents hydrogen atom, a methyl group or -COOX³, X¹, X² and X³ each independently represent hydrogen atom, an alkali metal, an alkaline earth metal, an ammonium group or an ammonium group substituted by an organic group, and n represents 0 or 1, provided that when n represents 0, R⁵ does not represent -COOX³.

[0020] In the above formula (3), R⁶ represents hydrogen atom or a methyl group, R⁷ represents a linear alkylene group having from 1 to 4 carbon atoms or a branched alkylene group, X⁴ represents -CONH- or -COO-, and X⁵ represents hydrogen atom, an alkali metal, an alkaline earth metal, an ammonium group or an ammonium group substituted by an organic group.

[0021] In the present invention, the ratio of the copolymer (B) in the cement admixture to the fresh cement composition in terms of the solid content of cement admixture is preferably from 0.1 to 20 mass%, more preferably from 0.5 to 10 mass%. If the content ratio is less than 0.1 mass%, a fresh cement composition may not be imparted with a sufficiently high viscosity and readily undergo the material separation, whereas if it exceeds 20 mass%, a fresh cement composition may not be imparted with satisfactory fluidity and good fluidity retentive property.

[0022] Examples of the N-vinylcarboxylic acid amide-type monomer (a) represented by the formula (1) used as component (B) (that is, (B₁) and (B₂)) in the cement admixture of the present invention include N-vinylformamide, N-vinylacetamide, N-methyl-N-vinylformamide and N-methyl-N-vinylacetamide. Among these, N-vinylacetamide is preferred.

[0023] The copolymerization compositional ratio of the N-vinylcarboxylic acid amide-type monomer (a) represented by formula (1) to the copolymer (B) is from 30 to 90%, preferably from 40 to 80%, and more preferably from 50 to 70%. If this ratio exceeds 90%, a fresh cement composition cannot be imparted with satisfactory fluidity and good fluidity retentive property, whereas if it is less than 30%, a fresh cement composition may not be imparted with a sufficiently high viscosity and readily undergo the material separation.

[0024] Examples of the unsaturated carboxylic acid-type monomer represented by formula (2) include (meth)acrylic acid, crotonic acid, isocrotonic acid, maleic acid, fumaric acid, itaconic acid and salts thereof. The term "(meth)acryl" as used herein means both "acryl" and "methacryl".

[0025] Examples of the salt of unsaturated carboxylic acid include an alkali metal salt such as sodium and potassium, an alkaline earth metal salt such as calcium and magnesium, an ammonium salt, and an ammonium salt substituted by an organic group, such as methylamine, ethylamine, dimethylamine, diethylamine and triethylamine. Among these, preferred are an alkali metal salt, an ammonium salt and an ammonium salt substituted by an organic group.

[0026] In the present invention, examples of the unsaturated sulfonic acid-type monomer represented by formula (3) used as the other component of the anionic unsaturated monomer in the copolymer component (B) include 2-(meth)acrylamido-2-methylpropanesulfonic acid, 2-(meth)acrylamidoethanesulfonic acid, (meth)acrylic acid methanesulfonic acid, 2-(meth)acrylic acid ethanesulfonic acid, 3-(meth)acrylic acid propanesulfonic acid and salts thereof. Among these, (meth)acrylates and 2-acrylamido-2-methylpropane sulfonates are preferred. Examples of the salt include an

BEST MODE FOR CARRYING OUT THE INVENTION

[0037] The present invention is described in greater detail in below by referring to the Examples, Comparative Examples and Test Examples. However, the present invention is by no means limited to these Examples. Unless otherwise indicated specifically, % means mass%.

Production Example 1: Production of Copolymer

[0038] Into a glass-made reactor equipped with a stirrer, 200 g of an aqueous 20% sodium methacrylate (MAA-Na) solution was charged. Thereto, 740 g of water was added and then 60 g of N-vinylacetamide (NVA) and 0.01 g of ammonium thioglycolate were dissolved. Subsequently, in a constant temperature bath kept at 50°C, the dissolved oxygen was removed by passing nitrogen while stirring the solution and thereto, 0.45 g of 2,2'-azobis(2-amidinopropane) dihydrochloride (AAD) was added and reacted in the nitrogen stream to obtain an aqueous solution of Copolymer (B1). The weight average molecular weight of the copolymer obtained was 2,560,000.

Production Examples 2 to 9: Production of Copolymers

[0039] Aqueous solutions of Copolymer (B2) to (B9) were obtained in the same manner as in Production Example 1 except for changing the monomer composition and addition amount thereof. The weight average molecular weights thereof are shown in Table 1 below together with (B1).

[Table 1]

Name of Copolymer	Weight of Monomer Charged (g)							AAD (g)	Weight Average Molecular Weight ($\times 10^4$)
	Monomer A		Monomer B			Monomer C			
	NVA	NVF	20 wt% MAA-Na	20 wt% AA-Na	20 wt% AMPS-Na	MA	AN		
B1	60		200					0.45	256
B2	70			150				0.60	243
B3	50				250			0.60	248
B4	50		100		150			0.50	269
B5	50		200			10		0.35	223
B6	50		200				10	0.40	231
B7	50				200	10		0.50	240
B8	50				200		10	0.40	253
B9		50	200				10	0.35	234

NVA: N-vinylacetamide, NVF: N-vinylformamide, MAA-Na: Sodium methacrylate, AA-Na: sodium acrylate, AMPS-Na: sodium 2-acrylamido-2-methylpropanesulfonate, MA: methyl acrylate, AN: acrylonitrile, AAD: 2,2'-azobis(2-amidinopropane) dihydrochloride

Production Example 10: Preparation of cement admixture

[0040] Using MOLMASTER L-10 (trade name, produced by Showa Denko K.K.) as the sodium salt of melaminesulfonic acid formaldehyde condensate (MSF), Cement Admixture (S1) of the present invention was obtained by adding 9.6 g of the aqueous solution of Copolymer (B1) prepared in Production Example 1 to 100 g of the MOLMASTER L-10 such that the ratio of the solid content of the copolymer (B) to the solid content of the cement admixture was 3.0%, and then stirring and mixing the blend.

Production Examples 11 to 18: Preparation of cement admixture

[0041] Cement Admixtures (S2) to (S9) of the present invention were obtained in the same manner as in Production

Test Example

(1) Evaluation 1 of Performance of Cement Admixtures

[0045] In order to examine the performance of Cement Admixtures (S1) to (S18) obtained in Production Examples 10 to 27, each cement admixture was added at the preparation of a concrete and tests for evaluating the performance with respect to the fluidity, fluidity retentive property, self-filling property, material separation resistance and strength of the hardened form, were conducted.

[0046] Also, the cement admixture compositions obtained in Comparative Production Examples and the commercially available cement admixtures (R4), (R5), (R6) and (R7) on their individual sole use were tested in the same manner for evaluating the performance. The results are additionally shown as Comparative Examples.

R4: sodium salt of melaminesulfonic acid formaldehyde condensate (MOLMASTER L-10, trade name, produced by Showa Denko K.K.)

R5: sodium salt of naphthalenesulfonic acid formaldehyde condensate (MIGHTY-150, trade name, produced by Kao Corp.)

R6: lignin sulfonic acid salt (SUNFLOW KS, trade name, produced by San Flow K.K.)

R7: polycarboxylic acid (PARIK FP-100S, trade name, produced by Fujisawa Yakuhin K.K.)

(1-1) Blending of Concrete and Method for Kneading

(i) Blending of Concrete

[0047] The materials blended in the concrete for the performance evaluation tests are shown in Table 3. Here, an AE agent VINSOL (trade name, produced by Sanso Kagaku K.K.) was used to have a target air content of 4.5%. Furthermore, the amount of the cement admixture added was adjusted by setting the target flow value to $60 \text{ cm} \pm 3 \text{ cm}$.

[Table 3]

W/C (%)	S/a ⁵⁾ (%)	Unit Amount (kg/m ³)			
		W ¹⁾	C ²⁾	S ³⁾	G ⁴⁾
50.0	52.3	175	350	920	846

1) Water (W): tap water

2) Cement (C): ordinary Portland cement (specific gravity: 3.16)

3) Small aggregate (S): river sand from Sagami river (specific gravity: 2.63, fineness modulus: 2.71)

4) Giant aggregate (G): crushed stone from Ohme (specific gravity: 2.65, fineness modulus: 6.85)

5) a=S+G

(ii) Method for Kneading

[0048] The cement, small aggregate and giant aggregate each in a predetermined amount were charged into a 50 L-volume forced twin screw mixer and stirred for 30 seconds. Thereafter, a mixed solution of water, AE agent and cement admixture was added thereto and the resulting blend was stirred for 90 seconds, discharged and subjected to the performance tests.

(1-2) Method for Carrying Out Performance Tests

(i) Fluidity Test

Slump flow test:

[0049] This was carried out in accordance with JASS (Nippon Kenchiku Gakkai (Japan Architecture Society Standard)) 5 T-503 and measured immediately after the kneading, after 30 minutes, after 60 minutes and after 90 minutes.

(ii) Self-Filling Property Test

[0050] Using an L-type tester shown in Fig. 1 (perspective view) and Fig. 2 (side view) in the state where the partition

[Table 4]

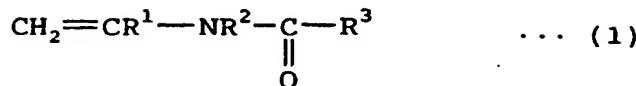
Section	No.	Cement Admixture		Slump Flow (cm)			Self-Filling Property (filling height) (cm)	Separation Resistance (internal/external coarse aggregate ratio)	Compressive Strength (N/mm ²)		
		Name	Amount Added (wt%)	Air Content (%)	Immediately After	After 30 min.	After 60 min.	After 90 min.	1 Day Age	7 Days Age	28 Days Age
	1	S1	1.36	4.7	60.0	60.5	60.0	59.0	15.5	1.06	11.9
	2	S2	1.42	4.5	58.5	58.5	58.0	57.5	14.0	1.04	11.5
	3	S3	1.30	4.5	60.5	60.0	60.0	59.0	15.5	1.08	11.8
	4	S4	1.30	4.6	60.0	59.5	59.0	58.5	15.0	1.08	12.2
	5	S5	1.36	4.5	59.5	60.0	59.0	58.0	15.5	1.09	12.1
	6	S6	1.36	4.3	62.0	60.5	60.5	60.0	16.5	1.07	11.7
	7	S7	1.36	4.5	61.5	61.5	60.0	60.0	16.0	1.08	11.5
	8	S8	1.30	4.4	62.0	60.5	59.5	59.5	16.0	1.06	11.4
	9	S9	1.42	4.4	60.0	60.0	59.0	58.5	15.0	1.04	12.0
Example	10	S10	1.30	4.2	61.5	60.5	60.5	59.5	15.5	1.05	11.6
	11	S11	1.36	4.5	58.5	59.0	58.5	57.5	14.5	1.03	11.7
	12	S12	1.24	4.4	59.5	60.5	59.5	58.5	15.0	1.06	11.9
	13	S13	1.24	4.6	60.5	60.5	59.5	59.0	15.0	1.05	11.8
	14	S14	1.24	4.7	60.0	59.5	59.0	59.0	15.5	1.06	12.2
	15	S15	1.24	4.5	61.0	60.0	59.5	59.0	15.5	1.06	12.4
	16	S16	1.24	4.6	60.5	61.5	60.0	60.0	15.0	1.04	12.6
	17	S17	1.24	4.6	59.5	58.5	58.5	58.0	15.0	1.05	11.5
	18	S18	1.36	4.4	59.0	58.5	58.0	57.5	14.5	1.04	11.8
	19	R1	3.00	4.7	42.0	33.5	28.0	25.5	2.5	1.03	8.0
	20	R2	3.00	4.8	40.5	32.0	27.0	23.5	2.0	1.04	8.1
	21	R3	3.00	4.7	42.0	32.5	27.5	23.0	2.5	1.04	7.8
Comparative Example	22	R4	1.30	4.5	62.0	45.5	40.0	34.0	9.5	1.25	10.9
	23	R5	1.24	4.6	61.5	42.0	38.0	32.0	8.0	1.22	10.3
	24	R6	3.00	4.7	43.0	34.5	29.5	27.0	3.0	1.03	8.0
	25	R7	0.60	4.3	60.5	61.5	59.5	58.0	10.5	1.31	8.3

* The amount of cement admixture added: mass% of polymer solid content based on cement

[Table 6]

Section	No.	Cement Admixture Name	Amount Added (wt%)	Air Content (%)	Slump Flow (cm)			Compressive Strength (N/mm²)		
					Immediately After min.	After 30 min.	After 60 min.	1 Day Age	7 Days Age	28 Days Age
	1	S1	0.75	4.3	20.3	19.6	18.9	7.2	19.5	33.4
	2	S2	0.75	4.4	19.8	19.1	18.6	6.3	18.9	32.4
	3	S3	0.75	4.6	20.9	19.9	19.1	6.4	17.3	32.4
	4	S4	0.75	4.5	20.8	19.7	18.8	7.4	19.9	33.5
	5	S5	0.75	4.5	20.6	19.8	19.0	6.2	18.8	32.4
	6	S6	0.75	4.4	20.7	19.5	18.7	6.8	18.4	32.4
	7	S7	0.75	4.4	20.4	19.4	18.5	7.0	19.0	32.8
	8	S8	0.75	4.5	20.6	19.7	19.0	6.5	17.3	32.3
	9	S9	0.75	4.5	19.7	19.0	18.0	7.1	19.2	32.8
Example	10	S10	0.75	4.6	20.9	19.6	18.7	6.9	18.4	32.4
	11	S11	0.75	4.3	20.4	19.4	18.6	6.7	17.7	32.5
	12	S12	0.75	4.5	21.4	20.2	19.3	6.8	18.8	32.9
	13	S13	0.75	4.4	21.1	20.2	19.2	6.9	18.4	32.5
	14	S14	0.75	4.4	21.2	19.9	19.0	7.2	19.0	33.0
	15	S15	0.75	4.7	21.0	19.7	18.8	6.1	17.3	32.2
	16	S16	0.75	4.5	20.5	19.2	18.4	6.6	19.2	33.1
	17	S17	0.75	4.6	21.1	19.8	19.0	6.6	18.4	32.8
	18	S18	0.75	4.5	20.2	18.9	18.4	6.4	17.7	32.3
	19	R1	1.60	4.6	20.2	10.7	7.5	5.5	15.0	27.7
	20	R2	1.60	4.7	20.0	10.7	7.7	5.3	15.2	28.0
Comparative Example	21	R3	1.60	4.6	19.6	10.2	7.2	5.3	15.3	27.8
	22	R4	0.75	4.5	21.6	13.0	9.5	5.6	15.5	28.7
	23	R5	0.75	4.6	21.7	12.7	8.8	5.5	15.2	27.9
	24	R6	1.60	4.6	20.4	11.0	8.2	5.4	15.5	28.3
	25	R7	0.35	4.3	21.1	20.0	18.6	4.9	14.2	26.6

* The amount of cement admixture added: mass% of polymer solid content based on cement



5 wherein the symbols have the same meanings as in claim 1,

(b) from 10 to 70 mass% of one or more anionic unsaturated monomer selected from an unsaturated carboxylic acid-type monomer represented by the following formula (2)



10 wherein the symbols have the same meanings as in claim 1 and
15 an unsaturated sulfonic acid-type monomer represented by the following formula (3)

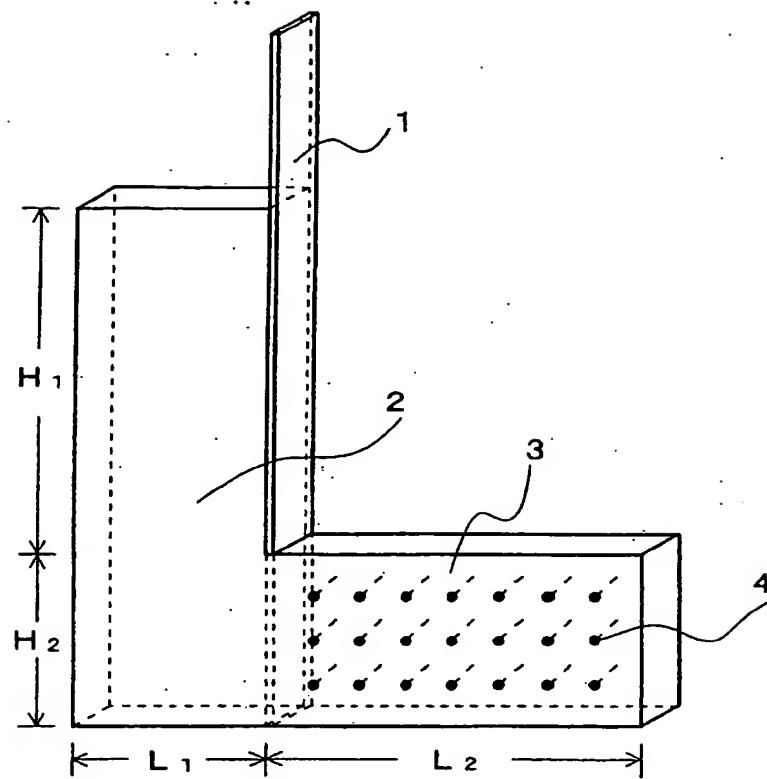


wherein the symbols have the same meanings as in claim 1 and

25 (c) from 0 to 40 mass% of one or more nonionic unsaturated monomer,
provided that the total of (a), (b) and (c) is 100 mass%.

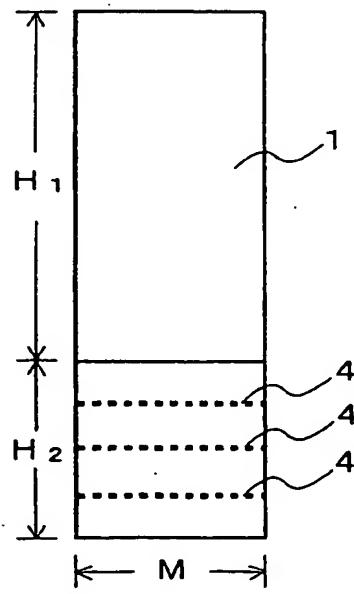
3. The cement admixture as claimed in claim 1 or 2, wherein the content ratio of the copolymer (B_1) or (B_2) in the solid content of the cement admixture is from 0.1 to 20 mass%.
- 30 4. The cement admixture as claimed in claim 1 or 2, wherein the N-vinylcarboxylic acid amide-type monomer (a) is N-vinylacetamide.
- 35 5. The cement admixture as claimed in claim 1 or 2, wherein the anionic unsaturated monomer (b) is one or more monomer selected from acrylic acid, methacrylic acid, maleic acid, 2-acrylamido-2-methylpropanesulfonic acid and salts thereof.
6. The cement admixture as claimed in claim 2, wherein the nonionic unsaturated monomer (c) is one or more monomer selected from alkyl acrylates, alkyl methacrylates, hydroxyalkyl acrylates, hydroxyalkyl methacrylates, acrylonitrile, methacrylonitrile and vinyl acetate.
7. The cement admixture as claimed in claim 2 or 6, wherein the ratio of the nonionic unsaturated monomer (c) in the copolymer (B_2) is from 5 to 30 mass%.
- 45 8. A method for preparing a cement composition, comprising adding a cement admixture described in any one of claims 1 to 7 to a cement composition slurry.
9. The method for preparing a cement composition as claimed in claim 8, wherein the compound (A) and the copolymer (B_1) or (B_2) are separately added.
- 50 10. The method for preparing a cement composition as claimed in claim 8 or 9, wherein the addition amount of the cement admixture is from 0.1 to 5.0 mass% in terms of the solid content based on the cement composition.
11. A cement composition obtainable by the preparation method described in any of claims 8 to 10.
- 55 12. A cement composition having blended therein a cement admixture described in any one of claims 1 to 7.
13. A hardened product of concrete or mortar using a cement composition described in claim 12.

Fig. 1



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Fig. 2



**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 00 12 7803

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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